COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one oxidation base, at least one 3-aminopyridine derivative as direct dye, and at least one substituted meta-aminophenol as coupler, as well as to the dyeing process using this composition.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as regards the oxidation bases and couplers allows a wide range of colours to be obtained.

It is also known that, in order to vary the shades obtained even more and to give them glints, it is possible to use, in combination with the oxidation dye precursors and couplers, direct dyes, i.e. coloured substances which provide a coloration in the absence of an oxidizing agent.

The great majority of these direct dyes belong to the family of nitrobenzene compounds and have the drawback, when they are incorporated into dye compositions, of leading to colorations that are not sufficiently fast, in particular with respect to shampoos.

The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy a certain number of requirements. Thus, it must be able to give shades of the desired intensity and it must be able to withstand external agents (light, bad weather, washing, permanent-waving, perspiration and rubbing).

The dyes must also make it possible to cover white hair, and, finally, they must be as unselective as possible, i.e. they must give the smallest possible differences in colour all the way along the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

Compositions for the oxidation dyeing of keratin fibres containing a combination of a benzenic oxidation base, a direct dye of the 3-aminopyridine family and an unsubstituted meta-aminophenol as coupler have already been proposed, in particular in patent application FR-A-2,285,851. However, the colorations obtained using such compositions are not entirely satisfactory, in particular from the point of view of their chromaticity and their fastness.

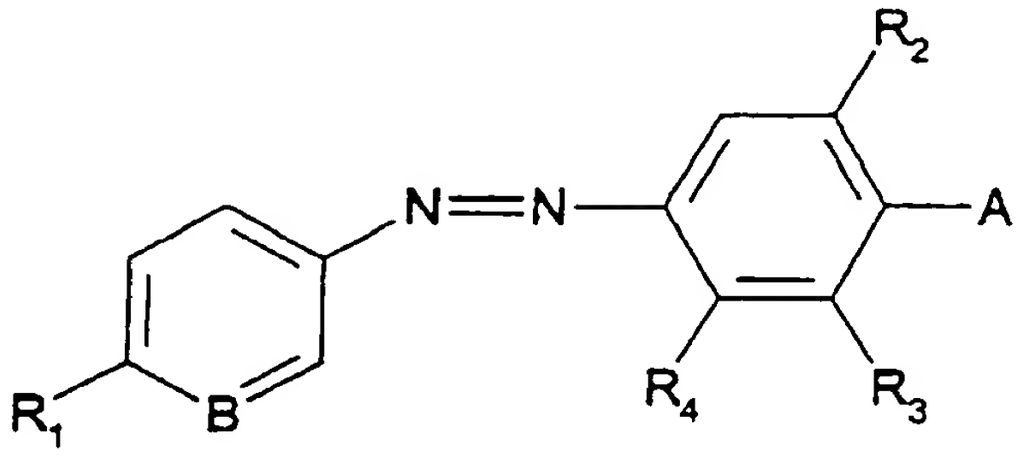
The Applicant has now discovered that it is possible to obtain novel dyes which are capable of giving intense and chromatic colorations, which show little selectivity and which satisfactorily withstand the various attacking factors to which the fibres may be subjected, by combining at least one oxidation base, at least one suitably selected 3-aminopyridine derivative as direct dye, and at least one suitably selected meta-aminophenol derivative.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base,

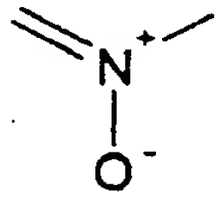
- as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I) below:



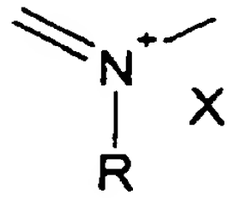
(I)

in which:

- B represents a group of formula (Ia) or (Ib) below:



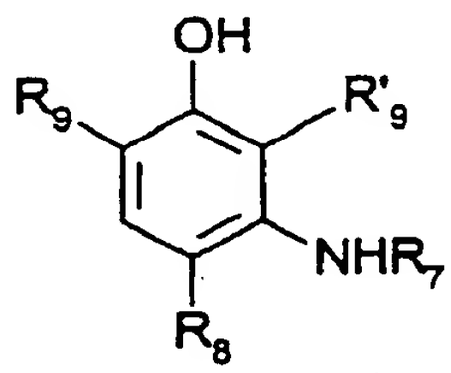
(Ia)



(Ib)

- R represents a C_1-C_4 alkyl radical;
- R_1 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;
- R_2 represents a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical;
- R_4 represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C_1-C_4 alkyl, nitro, amino or (C_1-C_4)acylamino radical;
- R_3 represents a hydrogen atom or else R_4 and R_3 together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;

- A represents a residue $-NR_5R_6$ in which R_5 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical; R_6 represents a hydrogen atom, a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical, a phenyl ring or a $-CH_2-SO_3Na$ radical;
- X^- represents a monovalent or divalent anion and is preferably chosen from a halogen atom such as chlorine, bromine, fluorine or iodine, a hydroxide, a hydrogen sulphate or a $(C_1$-$C_6)$alkyl sulphate such as, for example, a methyl sulphate or an ethyl sulphate, and
- at least one coupler chosen from the meta-aminophenol derivatives of formula (II) below, and the addition salts thereof with an acid:



(II)

in which:

- R_7 represents a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl or C_1-C_4 monoaminoalkyl radical;
- R_8 represents a hydrogen atom, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,

- R_9 and R'_9, which may be identical or different, represent a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 monohydroxyalkoxy or C_2-C_4 polyhydroxyalkoxy radical;

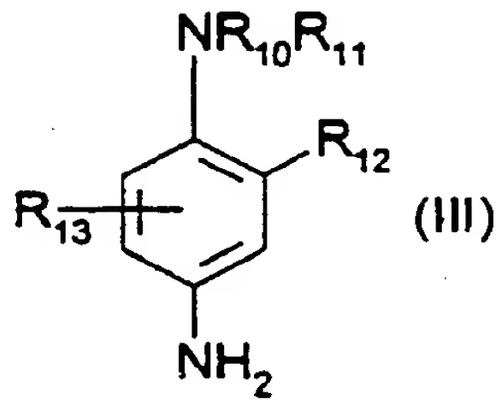
it being understood that at least one of the radicals R_7, R_8, R_9 and R'_9 is other than a hydrogen atom.

The dye composition in accordance with the invention gives intense, chromatic colorations which show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather, and with respect to perspiration and the various treatments to which the hair may be subjected. These properties are particularly noteworthy as regards the chromaticity.

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this dye composition.

The nature of the oxidation base(s) used in the ready-to-use dye composition is not critical. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

Among the para-phenylenediamines which can be used as oxidation base in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (III) below, and the addition salts thereof with an acid:



(III)

in which:

- R_{10} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, C_1-C_4 alkyl radical substituted with a nitrogenous group, phenyl or 4'-aminophenyl;
- R_{11} represents a hydrogen atom or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical, (C_1-C_4)alkoxy(C_1-C_4)alkyl radical or C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_{12} represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, or a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_1-C_4 hydroxyalkoxy radical, acetylamino(C_1-C_4)alkoxy, mesylamino(C_1-C_4)alkoxy or carbamoylamino(C_1-C_4)alkoxy radical,
- R_{13} represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

Among the nitrogenous groups of formula (III) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino,

tri(C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

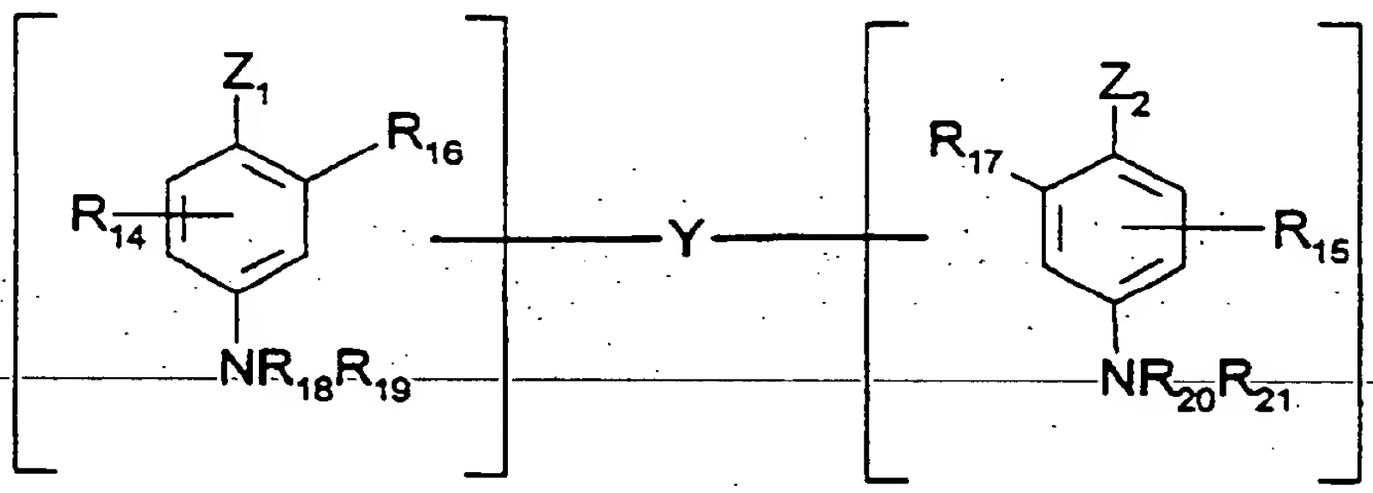
Among the para-phenylenediamines of formula (III) above, mention may be made more particularly of para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine and N-(β-methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

Among the para-phenylenediamines of formula (III) above, the ones most particularly preferred are

para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid.

According to the invention, the term "double bases" means compounds comprising at least two aromatic nuclei on which amino and/or hydroxyl groups are borne.

Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to the formula (IV) below, and the addition salts thereof with an acid:



(II)

in which:

- Z_1 and Z_2, which may be identical or different, represent a hydroxyl or $-NH_2$ radical which can be substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

- the linker arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with one or more nitrogenous groups and/or with one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals;
- R_{14} and R_{15} represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, C_1-C_4 monohydroxyalkyl radical, C_2-C_4 polyhydroxyalkyl radical or C_1-C_4 aminoalkyl radical or a linker arm Y;
- R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21}, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1-C_4 alkyl radical;

it being understood that the compounds of formula (IV) comprise only one linker arm Y per molecule.

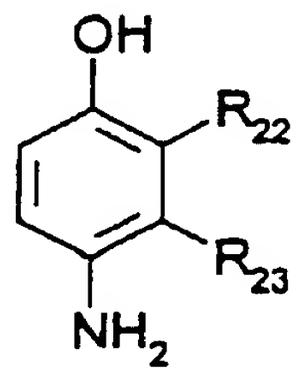
Among the nitrogenous groups of formula (IV) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, tri(C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

Among the double bases of formula (IV) above, mention may be made more particularly of N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)-

tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

Among these double bases of formula (IV), N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

Among the para-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (V) below, and the addition salts thereof with an acid:



(V)

in which:

- R_{22} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4)alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,

- R_{23} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, cyano(C_1-C_4)alkyl or (C_1-C_4)alkoxy(C_1-C_4)alkyl radical,

it being understood that at least one of the radicals R_{22} and R_{23} represents a hydrogen atom.

Among the para-aminophenols of formula (V) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocylic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in GB patents 1,026,978 and 1,153,196, such as 2-5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2,359,399 or Japanese patents JP 88-169,571 and JP 91-333,495 or patent applications WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-traminopyrimidine, and pyrazolopyrimidine derivatives, such as those mentioned in patent application FR-A-2,750,048 and among which mention may be made of pyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-

hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5, N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists, and the addition salts thereof with an acid.

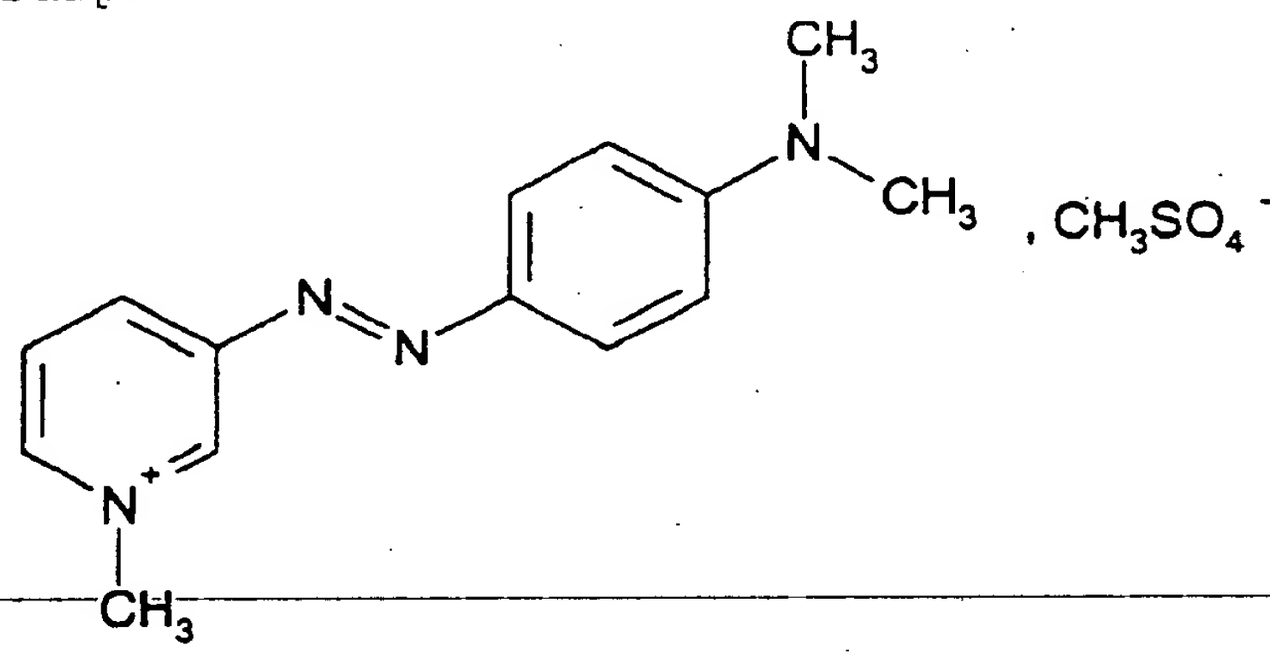
Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3,843,892 and DE 4,133,957 and patent applications WO 94/08969, WO 94/08970, FR-A-2,733,749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,

3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

The oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition in accordance with the invention, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

The 3-aminopyridine derivative(s) of formula (I) in accordance with the invention is (are) preferably chosen from:

- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



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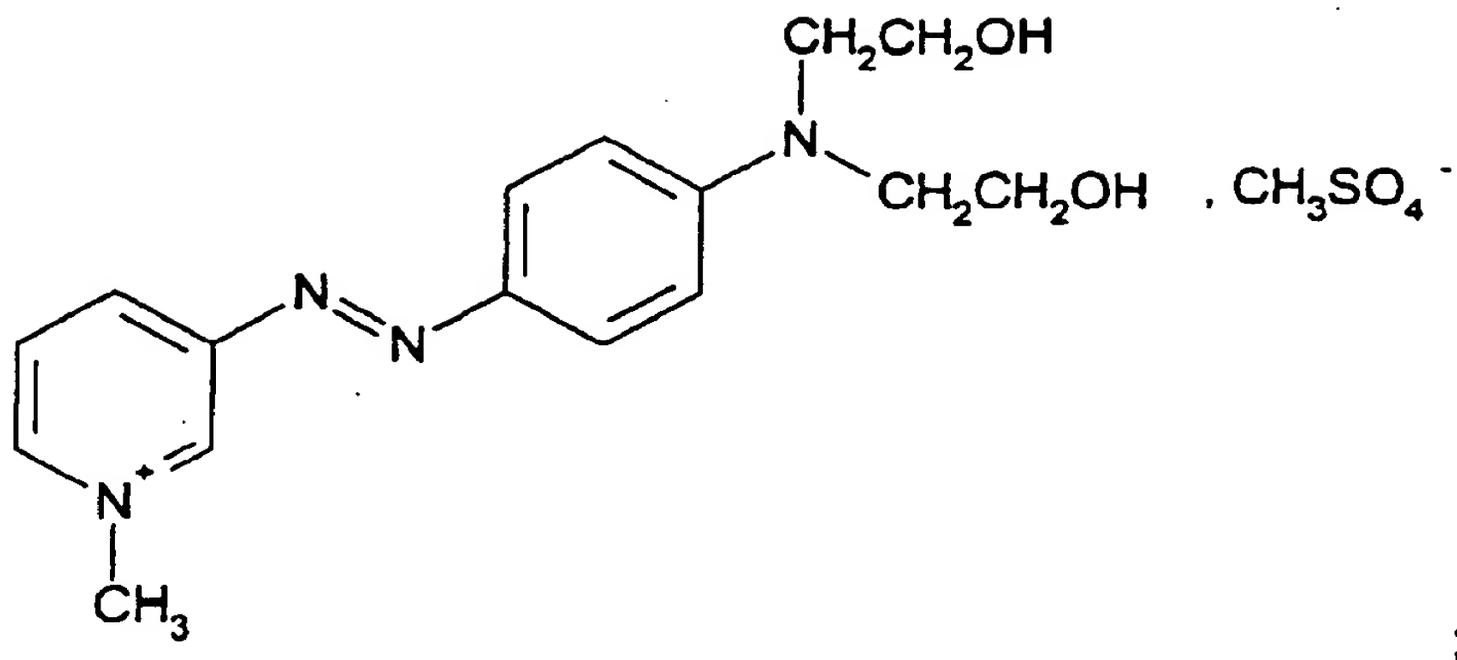
- 4'-bis(β-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



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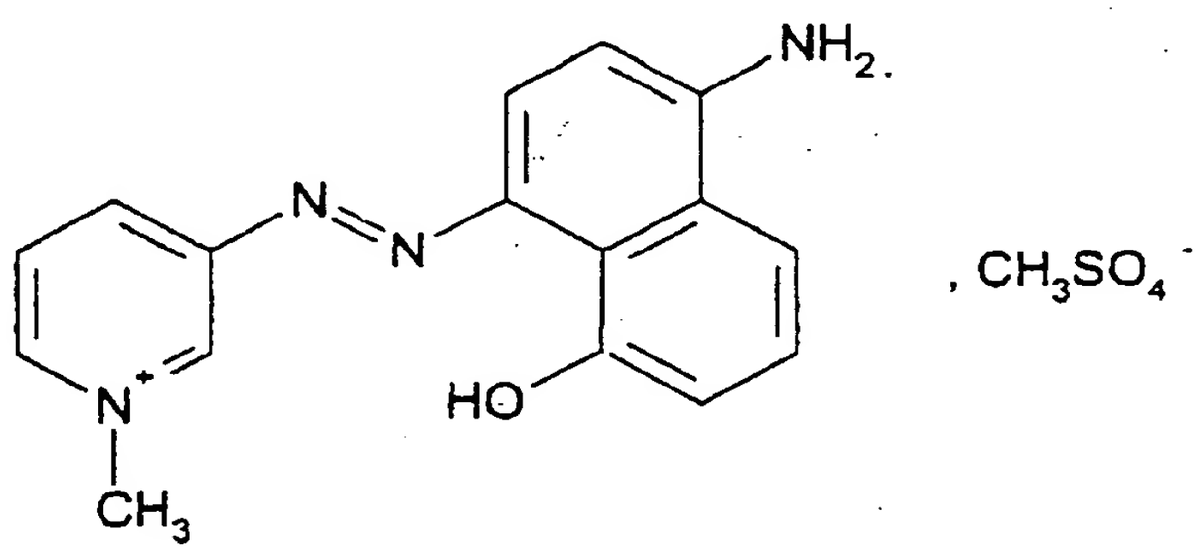
- 4'-amino-8'-hydroxynaphthalene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



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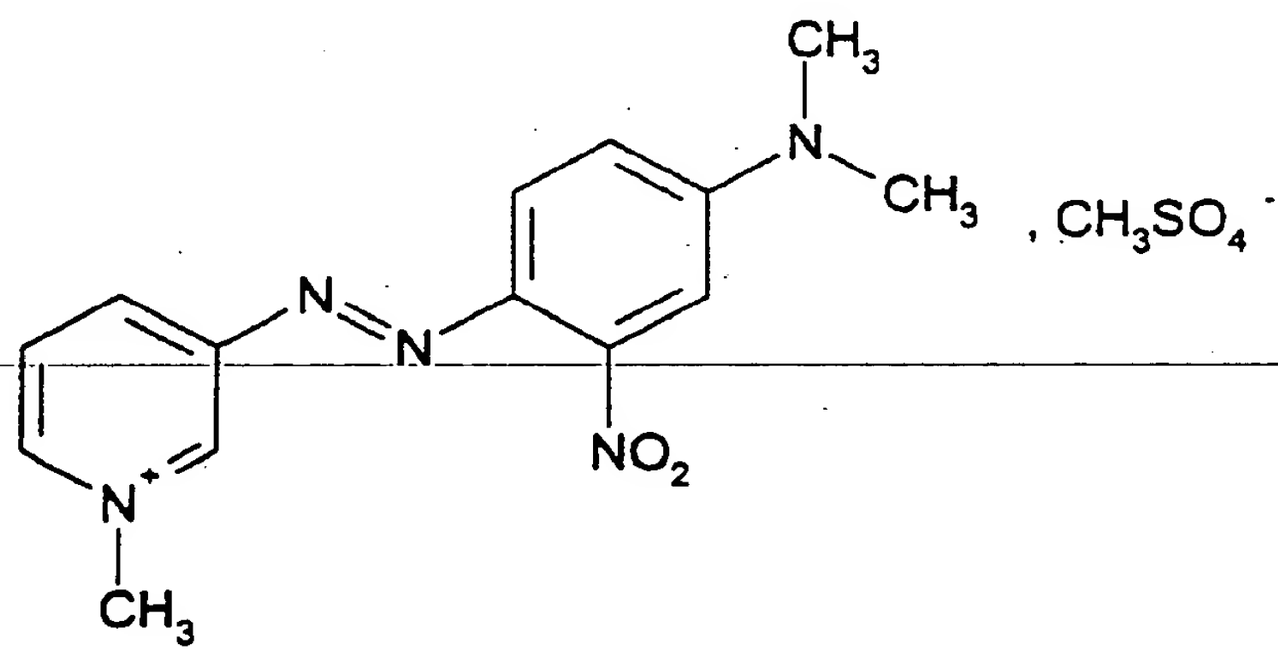
- 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



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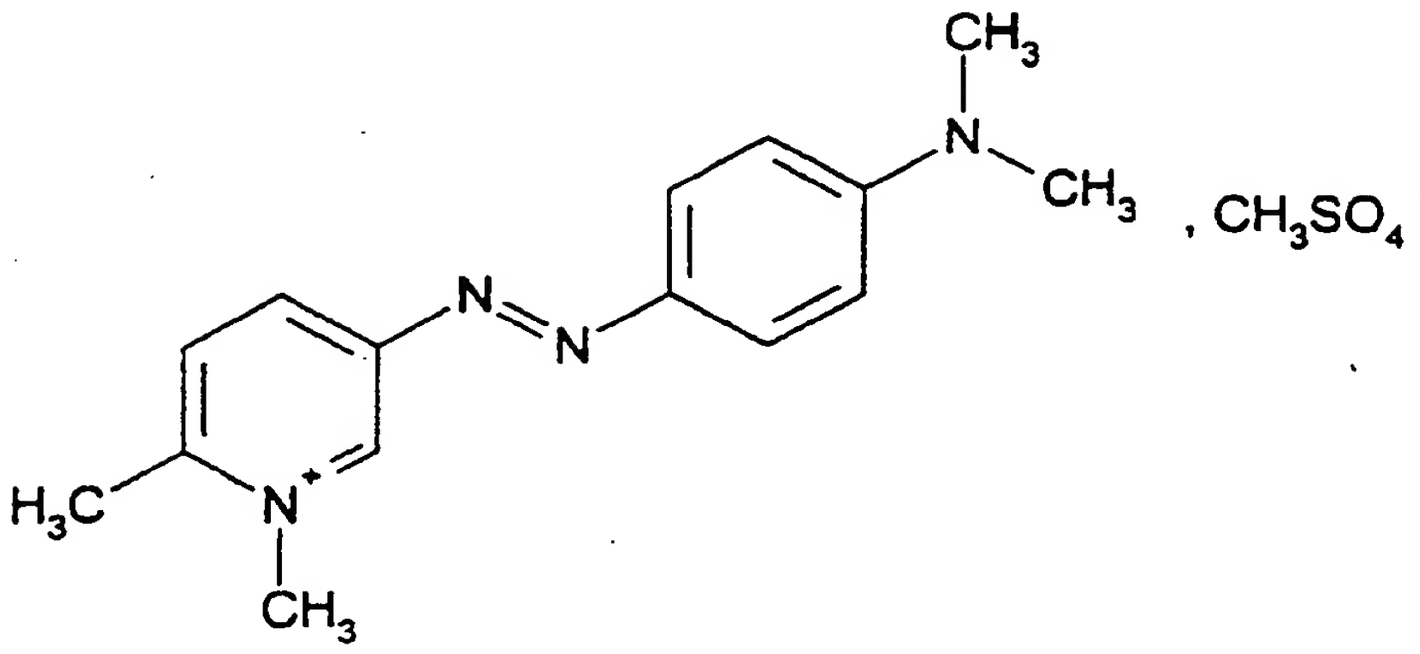
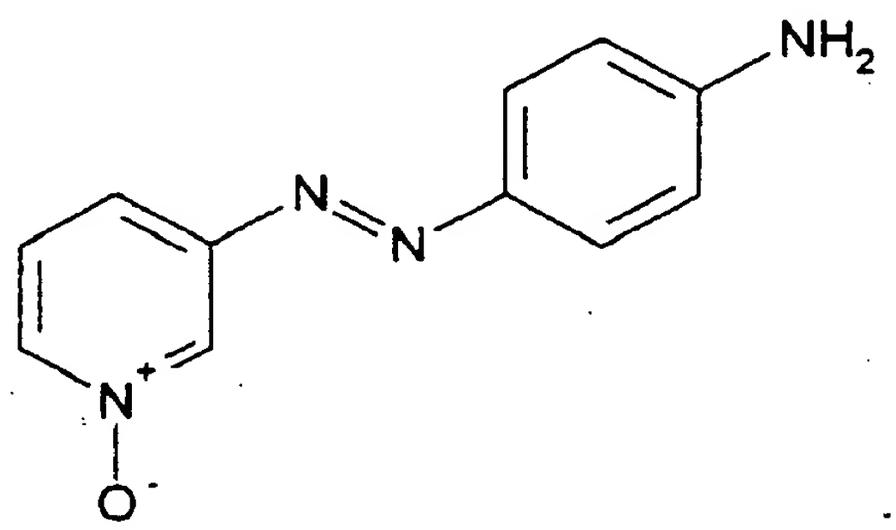
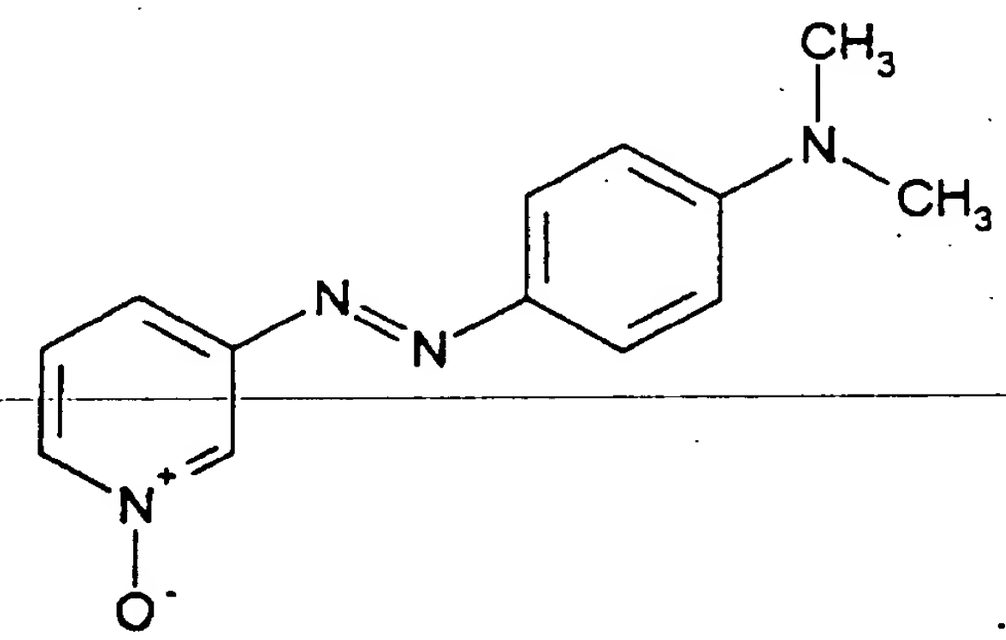
- 4'-dimethylaminobenzene-1'-azo-1,6-dimethyl-3-pyridinium methosulphate of formula:



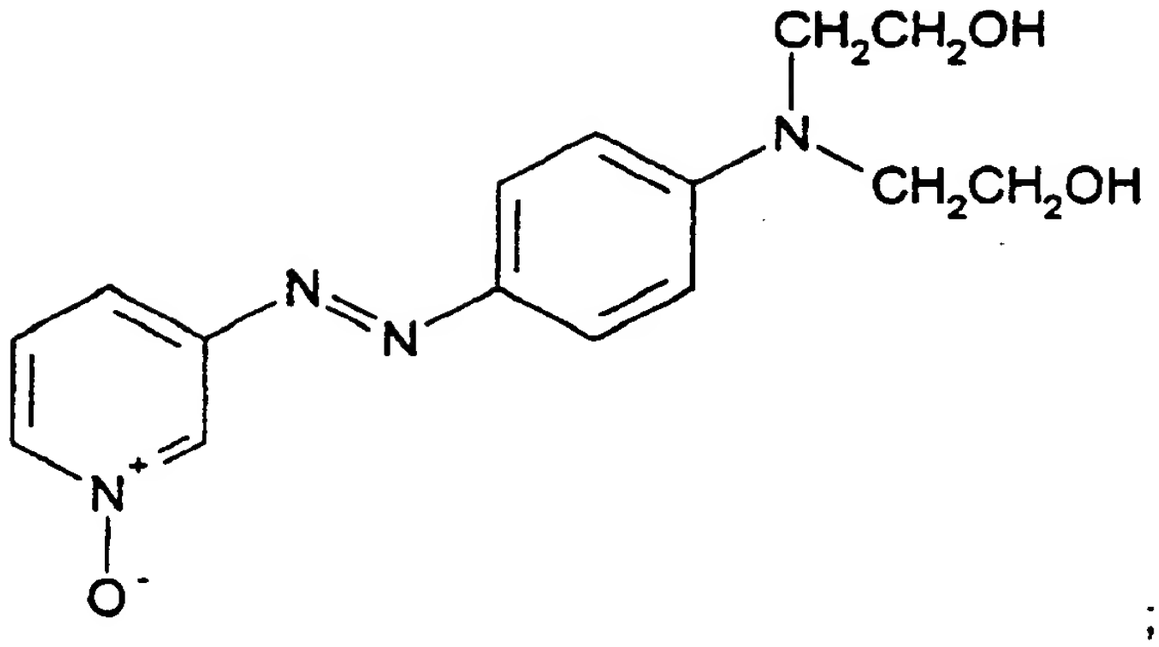
- 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:



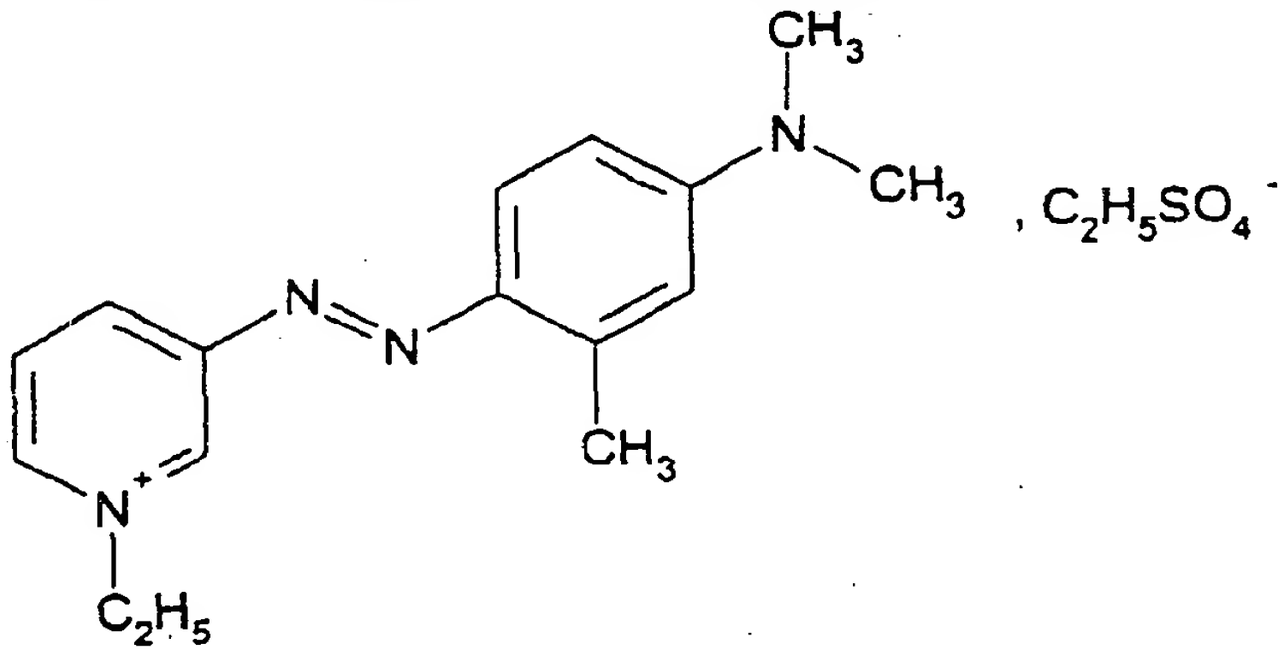
- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:



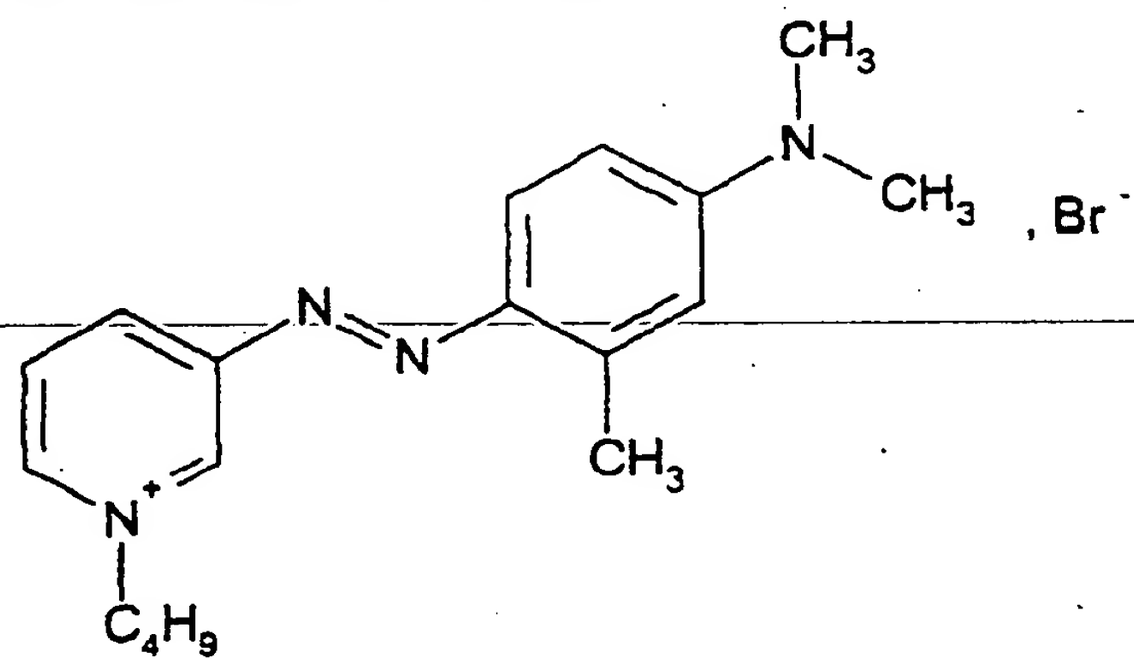
- 4'-N,N-bis(β-hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:



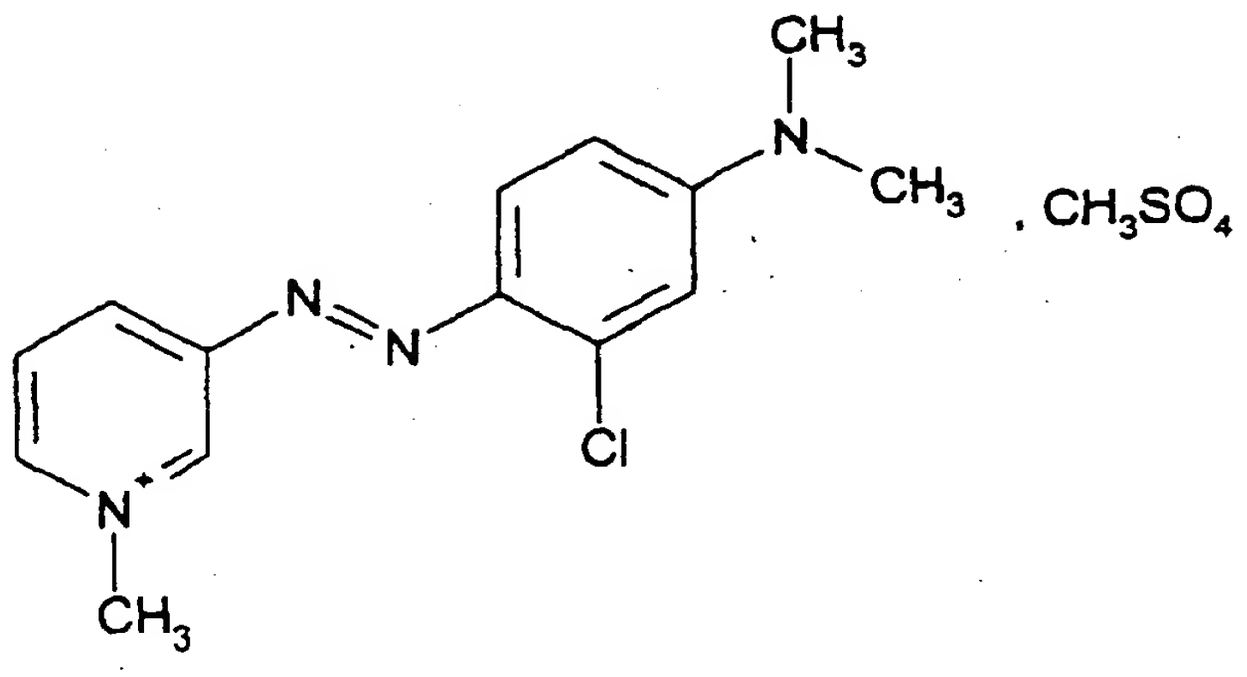
- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



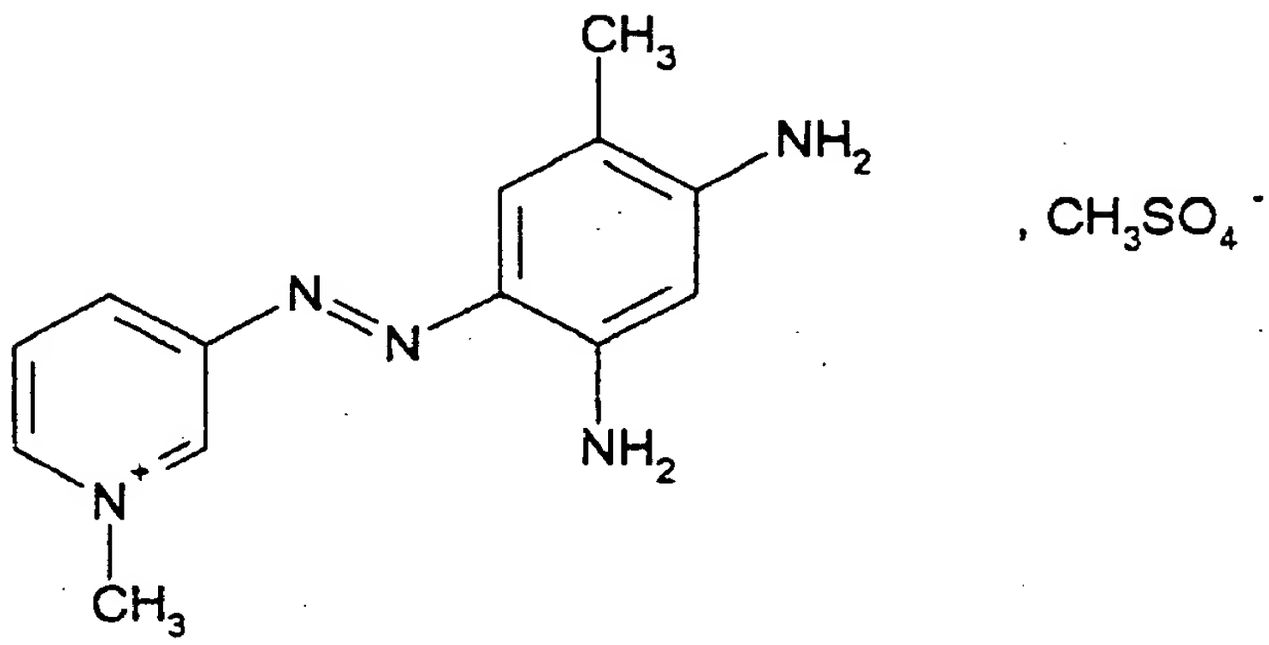
- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:



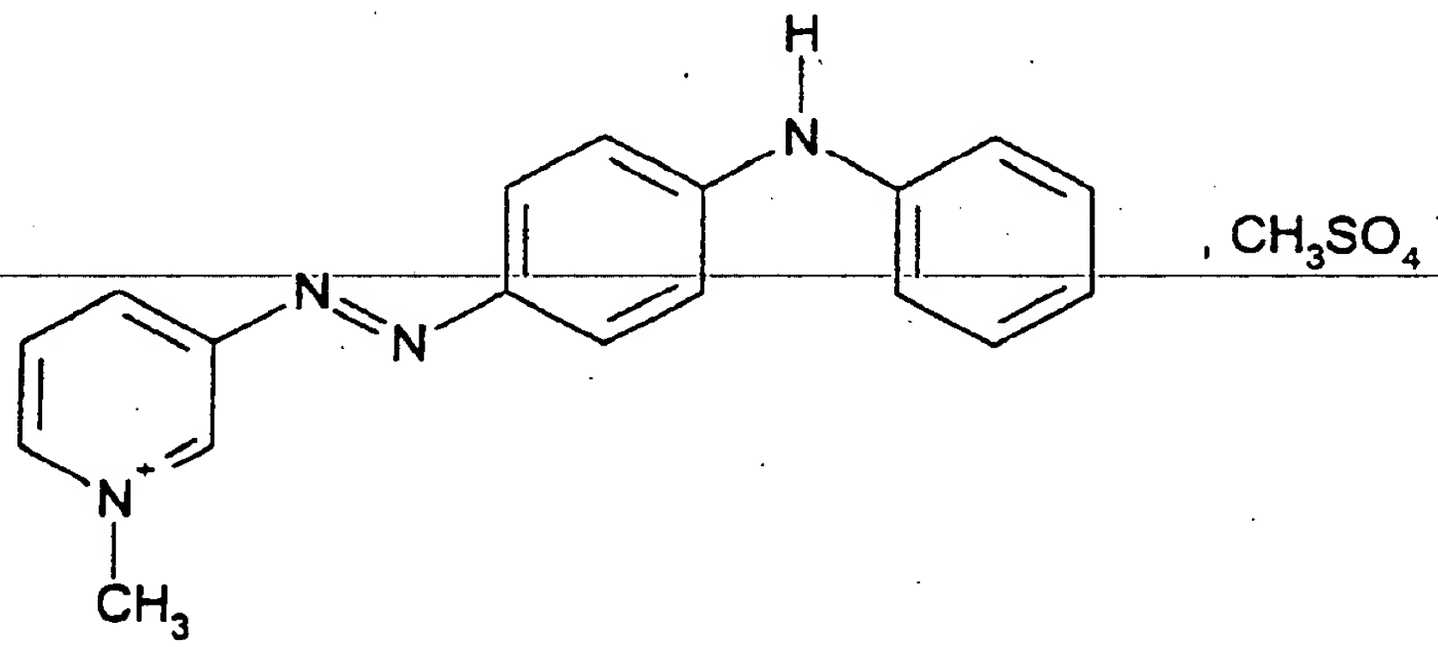
- 4'-dimethylamino-2'-chlorobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



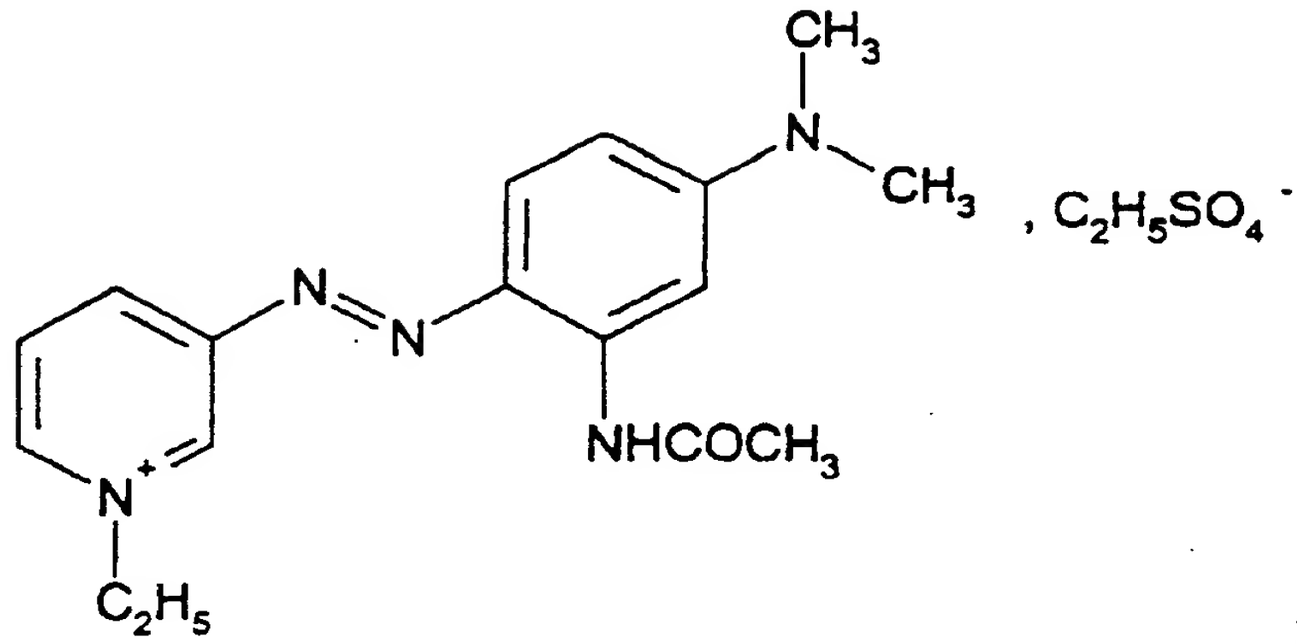
- 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



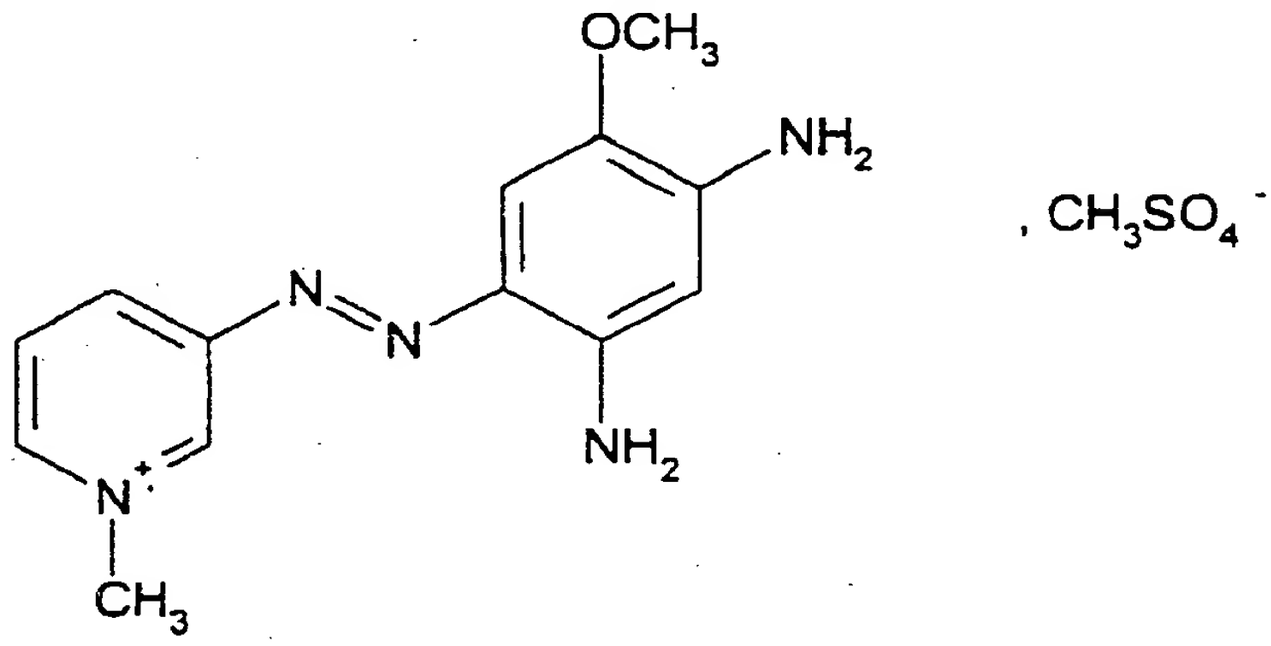
- 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:

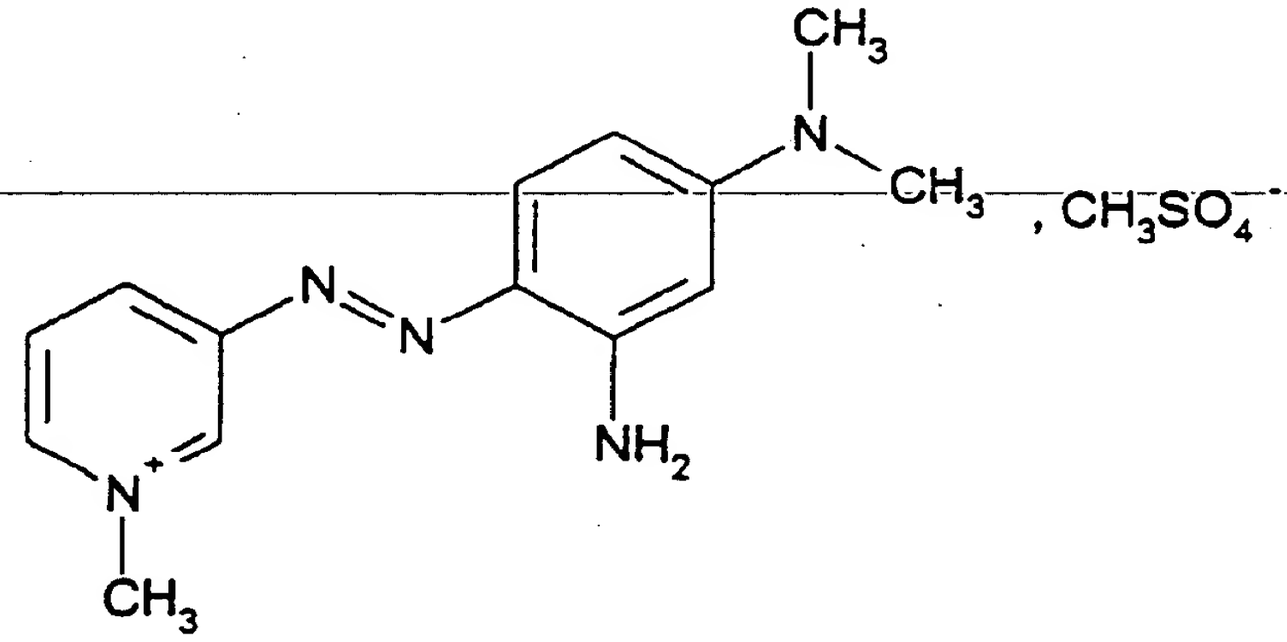


- 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



and

- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



The 3-aminopyridine derivative(s) of formula (I) used according to the invention preferably

represent(s) from 0.001 to 10% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.01 to 5% by weight approximately relative to this weight.

Among the meta-aminophenols of formula (II) above, mention may be made more particularly of 5-amino-2-methoxyphenol, 5-amino-2-(β-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-(γ-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol and 3-(β-aminoethyl)amino-6-chlorophenol, and the addition salts thereof with an acid.

The meta-aminophenol derivative(s) of formula (II) in accordance with the invention preferably represent(s) from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

The dye composition in accordance with the invention can also contain one or more couplers other than the meta-aminophenol derivatives of formula (II) and/or one or more direct dyes other than the 3-aminopyridine derivatives of formula (I), in

particular to modify the shades or to enrich them with glints.

Among the couplers which may also be present in the dye composition in accordance with the invention, mention may be made in particular of meta-phenylenediamines, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

When they are present, these additional couplers preferably represent from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidaticn bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) for the dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. Organic solvents which may be mentioned, for example, are C_1-C_4 alkanols, such as ethanol and isopropanol.

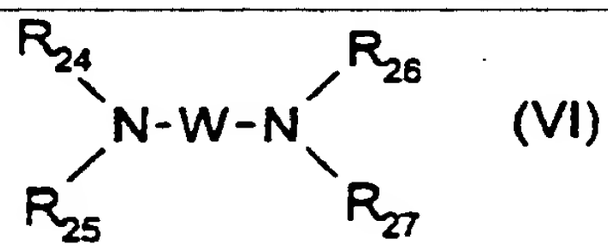
The solvents can be present in proportions preferably of between 1 and 40% by weight approximately

relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately, and preferably between 5 and 12 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine, 2-methyl-2-aminopropanol and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VI) below:



(VI)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_{24}, R_{25}, R_{26} and R_{27}, which may be identical or

different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl radical.

The dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair.

Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the advantageous properties intrinsically associated with the dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition or additions envisaged.

The dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which are optionally pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the dye composition as defined above.

According to this process, the dye composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing agent which is added to the dye composition only at the time of use, or which is present in an oxidizing composition that is

applied simultaneously or sequentially in a separate manner.

According to a particularly preferred embodiment of the dyeing process according to the invention, the dye composition described above is mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibres and is left on them for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

The oxidizing agent present in the oxidizing composition as defined above can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates, percarbonates and persulphates, peracids, enzymes such as 2-electron oxidoreductases, peroxidases and lactases. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such that, after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and

even more preferably between 5 and 11. It is adjusted to the desired value by means of acidifying or basifying agents usually used for dyeing keratin fibres and are as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

Another subject of the invention is a multi-compartment dyeing device or multi-compartment dyeing "kit", or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above and a second compartment of which contains the oxidizing composition as defined above. These devices may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

The examples which follow are intended to illustrate the invention without thereby limiting its scope.

EXAMPLES

COMPARATIVE DYEING EXAMPLES 1 TO 4

The dye compositions below were prepared (contents in grams):

EXAMPLE	1	2(*)	3	4(*)
4'-Dimethylaminobenzene-1'-azo-3-pyridine N-oxide (compound of formula (I))	0.5	0.5	-	-
2'-Acetylamino-4'-dimethyl-aminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate (compound of formula (I))	-	-	0.6	0.6
para-Phenylenediamine (oxidation base)	0.324	0.324	0.324	0.324
5-Amino-2-methylphenol (coupler of formula (II))	0.369	-	0.369	-
meta-Aminophenol (coupler)	-	0.327	-	0.327
Common dye support	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

(*): Comparative example not forming part of the invention

(**): Common dye support:

- Oleyl alcohol polyglycerolated with 2 mol of glycerol	4.0	g	
- Oleyl alcohol polyglycerolated with 4 mol of glycerol, containing 78% active material (A.M.)	5.69	g	A.M.
- Oleic acid	3.0	g	
- Oleylamine containing 2 mol of ethylene oxide, sold under the trade name Ethomeen O12® by the company Akzo	7.0	g	
- Diethylaminopropyl laurylaminosuccinamate, sodium salt, containing 55% A.M.	3.0	g	A.M.
- Oleyl alcohol	5.0	g	
- Oleic acid diethanolamide	12.0	g	
- Propylene glycol	3.5	g	
- Ethyl alcohol	7.0	g	
- Dipropylene glycol	0.5	g	
- Propylene glycol monomethyl ether	9.0	g	
- Sodium metabisulphite as an aqueous solution containing 35% A.M.	0.455	g	A.M.
- Ammonium acetate	0.8	g	
- Antioxidant, sequestering agent	qs		
- Fragrance, preserving agent	qs		
- Aqueous ammonia containing 20% NH_3	10.0	g	

Each of the dye compositions described above was mixed, at the time of use, with an equivalent

weight-amount of 20-volumes hydrogen peroxide (6% by weight) having a pH of about 3.

Each resulting mixture had a pH of about 10±0.2 and was applied for 30 minutes to locks of permanent-waved grey hair containing 90% white hairs.

The hair was then rinsed with water, washed with a standard shampoo, rinsed again and then dried.

The colour of the locks was evaluated before and after dyeing, in the Munsell system, using a Minolta CM 2002® spectrophotometer.

According to the Munsell notation, a colour is defined by the formula:

HV / C

in which the three parameters denote, respectively, the "Hue" or shade (H), the "Value" or intensity (V) and the "Chroma" or saturation (C), the oblique line simply being a convention and not denoting a ratio.

The increase in the coloration ΔE can be calculated by applying the Nickerson equation:

$$\Delta E = 0.4C_0dH + 6dV + 3dC$$

as described, for example, in "Journal of the Optical Society of America", vol. 34, No. 9, Sept 1944, pages 550-570.

In this equation, ΔE represents the difference in colour between two locks (in the present case the increase in the coloration), dH, dV and dC

represent the variation in absolute value of the three parameters H, V and C, C_0 representing the saturation of the lock relative to which it is desired to evaluate the difference in colour.

The greater the value of ΔE, the greater the difference in colour between the two locks, and, in the present case, the greater the increase in the coloration (or intensity of the coloration).

The results are given in the table below:

Example	Colour of the lock before dyeing	Colour of the lock after dyeing	Increase in coloration			
			dH	dV	dC	ΔE
1	3.3 Y 5.8/1.6	6.5 R 2.7/3.8	16.8	3.1	2.2	**36.0**
2 (*)	3.3 Y 5.8/1.6	1.2 YR 2.4/2.1	12.1	3.4	0.5	**29.6**
3	3.3 Y 5.8/1.6	5.1 R 2.5/3.0	18.2	3.3	1.4	**35.6**
4 (*)	3.3 Y 5.8/1.6	8.7 R 2.2/1.5	14.6	3.6	0.1	**31.2**

(*) Comparative example not forming part of the invention

It is found that the dye compositions of Examples 1 and 3 in accordance with the invention, i.e. compositions containing a combination of a direct dye of formula (I), an oxidation base and a coupler of formula (II), lead to more intense colorations than the dye compositions of Examples 2 and 4 not forming part

of the invention since they contain an unsubstituted coupler of meta-aminophenol type and as described, for example, in patent application FR-A-2,285,851.